GASOLINES CONTAINING DEPOSIT-REDUCING MONOAAMIDES OF POLYAMIDES CHARAC-
TERIZED BY IMPROVED WATER TOLERANCE

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ABSTRACT OF THE DISCLOSURE

An improved engine fuel for use in spark-ignition en-
gines, comprising a major proportion of gasoline and in
combination therewith a small amount of from about
0.0001 to about 0.1% by weight of an oil-soluble, emul-
sion-breaking reaction product of a polyamylene and a hydrocarbon monocarboxylic acid

(C_{15}-C_{20})

The present invention relates to an improvement in
motor fuels, specifically gasolines.

A large number of additives to gasoline have been
proposed in the past. Among them, additives aiming at
preventing, or at least substantially reducing, formation
and accumulation of deposits in the induction system
of automotive spark-ignition engines have been particu-
larly numerous. Some of these additives were found to
be quite effective in minimizing deposits, particularly
those deposits in the throttle body section of the engine's
carburetor, in the intake manifold, in the ports and on
the undersides of the valves. A number of these additives,
however, while effective in reducing deposits, introduced
new problems which hampered their acceptance by the
industry.

Many aminoalkylene amides and some of their salts,
found to be very effective as deposit-reducing additives
to gasoline, on being blended therewith in the presence
of water (and small quantities of moisture are practically
always present in systems for handling gasoline), fre-
quently cause a water haze because of the emulsification
occasioned by the additive. Particularly, at higher con-
centrations of the additive, if moisture is present with
the fuel, blending is often apt to cause formation of an
emulsion which separates on standing but very slowly.

A very striking example is presented by the blending
of mono-oleoylamide of N-2-hydroxyethyl-1,2-ethylenedi-
amine (oleic acid monoamide of N-2-hydroxyethyl-1,2-
ethylenediamine), an excellent, widely accepted, deposit-
reducing additive to motor gasoline. When this additive
is present in the rather small amount of 60 p.p.m. (60
parts per million parts of the base gasoline), haze occurs
when the fuel is mixed vigorously with water, although
the fuel settles bright within a period which may range
from a few minutes to several hours. A number of factors
influence the length of the time necessary for the resto-
ration of brightness, namely, the kind of base gasoline, the
amount and the quality of water present (e.g., pH and
concentrations of salts), as well as the intensity of agita-
tion in blending.

At higher concentrations, this difficulty becomes more
serious: the emulsion formed by agitation tends to per-
sist. At 250 p.p.m. concentration, for instance, in the
fuel, several days often may be required for the separa-
tion of distinct phases: an upper gasoline phase and a
lower clear aqueous phase at the bottom of the blend-
ing or storage tank.

One can readily perceive that the production of haze

in blending an additive into gasoline may be further
accentuated by its motion while being transported by
truck, ship or tank car from the refinery to distribution
outlets. Consequently, the gasoline must be settled to
be satisfactorily bright before it can be delivered to the
customer, and the time required for settling or brighten-
ting ties up tankage and delays the overall operations at
the distribution points.

For this reason, effort has been continued towards dis-
covering oil new deposit-reducing additives to gasoline
which would be substantially free of the aforementioned
emulsion-forming propensity or at least would require
but a short time for phase separation after the blending
or agitation during transportation and transfer of gaso-
line to storage tanks.

We have found that oil-soluble monoaamides of cer-
tain polyamines and certain organic acids are both effec-
tive in reducing the aforesaid deposit formation in
spark-ignition engines and are substantially free of the
emulsion and haze-forming tendencies of many other
oil-soluble amides; in other words, our monoaamides are
"emulsion-resistant." These particular monoaamides are
distinguishable from other oil-soluble amide additives
of the prior art by having been prepared by reacting alkyl-
ene polyamines or hydroxy-terminated alkylene poly-
amines, in each case containing from 2 to 10 carbon
atoms and at least two amino groups, with high molecu-
lar weight organic monocarboxylic acids in which the
hydrocarbon part of the acyl group is non-linear and non-
aromatic. More specifically, the amide additives of our
invention are produced by reacting a polyamine with either a highly branched ("multiple branched-chain")
allophatic hydrocarbon monocarboxylic acid of 12 to 30,
and preferably 15 to 30, carbon atoms in the molecule
and with at least two aliphatic radicals branching off the
main carbon chain, or with an alicyclic hydrocarbon
monocarboxylic acid of 12 to 30, and preferably 15 to
30, carbon atoms in its molecule having one or more
non-aromatic hydrocarbon rings. Suitable preferred
multiple branched-chain C_{15}-C_{20} hydrocarbon aliphatic
acids may carry two or more methyl or larger alkyl
radicals and may be either saturated or unsaturated. The
preferred alicyclic C_{15}-C_{20} hydrocarbon monocarboxylic
acids suitable for the making of the monoaamides prefer-
ably contain more than one hydrocarbon non-aromatic
ring, usually with 5 to 6 carbon atoms in the ring. The
acyclic hydrocarbon part of the acyl portion of these
acids may be attached to the carbonyl carbon by a hydro-
carbon chain, may carry alkyl substituents and may be
in the form of condensed rings.

As illustrative examples of the aforementioned multi-
ple branched-chain aliphatic acids, there may be listed:
2,2'-dimethyltetradecanoic acid, 2,3,5,7,9,11-hexamethyl
tetradecanoic acid, 2,3,5,7,9,11,13-heptamethylocoseneo-
adecanoic acid, 9,12-diethyltetradecanoic acid and the like. These acids may be obtained, for instance, by reacting
branched-chain polybutene or polypropene, e.g., their
trimers, tetramers, pentamers or hexamers, with an ester
of acrylic or methacrylic acid, as described in detail in

Another way to obtain the multiple branched-chain
aliphatic acids is by oxidizing in a known manner the
aldehydes formed in the reaction of carbon monoxide
with branched-chain olefins.

The C_{15}-C_{20} hydrocarbon alicyclic non-aromatic acids
suitable for the preparation of monoaamides operative
in accordance with our invention are exemplified by naph-
thenic acids, such as are recoverable from petroleum,
rosin acids (e.g., abietic acid), dioxyhexylhexane car-
bboxylic acid, 9-cyclohexyloctadecanoic acid, dextropimaric
acid, cholic acid, and the like.
The polyamines suitable for the preparation of the monoamide additives of the invention include:

- ethylenediamine,
- 2-hydroxyethylenediamine,
- diethylenetriamine,
- trimethylenediamine,
- propylenediamine,
- butylenediamine,
- 1,3-diamino-2-hydroxypropane,
- N-hydroxyethyl-1,3-diaminopropane,
- di-(trimethylene)triamine,
- N,N-di-(2-hydroxyethyl)ethylenediamine,
- N,N-di-(2-hydroxypropyl)trimethylenediamine,
- 2-hydroxypropyltrimethylenediamine,
- N-isopropylpropylenediamine,
- N-(2-hydroxypropyl)isobutylenediamine,
- N-[(hydroxy-t-butyloisobutylene diamine,
- N,N-dimethylenediamine,
- N,N-dialkylated diamine,
- 1-amino-2-hydroxy-3-dimethylaminopropane,
- N-2-aminoethylpiperazone,
- 2-piperazinyl ethanol,

and the like. For practical purposes, because of their availability in the trade, we prefer to use ethylenediamine, diethylenetriamine, propylenediamine, trimethylenediamine, and tetraethylenepentamine for the preparation of the amide additives of the invention.

We have found that by introducing into the gasoline (whether leaded or unleaded) intended for use in automobile engines from about 0.0002 to about 1.5% by weight, and preferably from about 0.0005 to about 1.0% by weight, of our particular kind of monoamide, the deposit-forming tendencies of the gasoline can be substantially reduced. At the same time the haze and emulsion-formation difficulties likely to arise in using other amide-type additives are noted to be essentially obviated. If any emulsification takes place at all, the emulsion breaks rapidly, gasoline becomes bright again, and water drops to the bottom of the blending tank in a matter of minutes, in all events in less than about 1 hour.

In actual practice we prefer to add the amide additive of our invention to gasoline in amounts from about 0.001 to about 0.1% by weight, that is, in proportions from about 10 to about 1,000 parts of the additive per 1 million parts of the gasoline.

The significant common property of the deposit-reducing monoamide additives of the present invention—whether the C₃₋₅₃ hydrocarbon portion of their acyl group is an aliphatic radical of at least two (and preferably more) alkyls branching off the main carbon chain or is an alicyclic configuration formed by one or more non-aromatic hydrocarbon rings—is their "emulsion resistance," that is, their proneness to facilitate a rapid separation of two distinct clear phases from aqueous emulsions which may be formed by agitating gasoline in the presence of water. This ability to permit a rapid phase separation is considered to be a unique characteristic of our monoamides as compared with analogous straight-chain aliphatic monoamides mentioned in the art.

This surprising property of the aliphatic amides as of our invention in not producing persistent, stable emulsions or haze when added to gasoline in the presence of water is persuasively demonstrated in a modification of the known ASTM D-1094 Test of "Water Reaction" or "Water Tolerance." In this modified procedure, 80 ml of gasoline and 20 ml of distilled water in a 100 ml graduated test-tube were thoroughly mixed by vigorous shaking for one minute; the time required for the two distinct bright phases (gasoline and water) to separate is then observed.

The preparation of the new emulsion-resistant monoamides for use in this test, effective in gasoline according to our invention, by reacting an alkyline polyamine or a hydroxy-substituted (or terminated) alkylene polyamine with a multiple branched-chain aliphatic monocarboxylic acid derived from trimers, tetramers, pentamers and hexamers of propene and butene is illustrated by the following example.

50 g. of methylacrylate is charged into a dry reaction flask provided with a reflux condenser protected with a CaCl₂ moisture trap, and 10 g. of anhydrous aluminum chloride is rapidly added while stirring. The aluminum chloride dissolves as the temperature is raised from 25 to 50° C. Then, 120 g. of a polypropene fraction boiling between 100 and 124° C. at 10 mm. Hg and averaging five propene groups per polymer molecule is added to the flask, and the contents are heated to 70–75° C. for five hours. Upon cooling to 30° C., 2 ml. of water and an excess of anhydrous sodium carbonate are added to destroy the aluminum chloride complex. The mixture is filtered through a Büchner funnel. To prevent polymerization of methylacrylate, 0.1 g. of hydroquinone is added, and volatiles are distilled to a bottoms temperature of 150° C. at a pressure of 5 mm. Hg. The remaining mixture is dissolved in 50 ml. of benzene, and saponified using 10 g. of sodium hydroxide, 20 ml. of water and 100 ml. of ethyl alcohol, and refluxed for three hours. The saponified mixture is acidified and extracted with hexane. Then, the hexane extract is water-washed to neutrality, and hexane is removed by distillation, leaving a mixture of carboxylic acids whose equivalent weight is 302 compared with 282 calculated for a mixture of acids averaging 18 carbon atoms. 16.6 g. of this acid product is mixed with 6.1 g. of hydroxyethyltrimethylammonium chloride in a flask arranged for refluxing. The amine is used in a slight molar excess. Next, toluene is added to the flask, and the mixture is refluxed for six hours. As a result, 2.0 ml. of water is removed, whereupon toluene is distilled off and the contents of the flask stripped to 160° C. at 5 mm. Hg. After cooling, water is added (2.0 ml), and the mixture is held eight hours at 60° C., during which time the imidazoline which is first formed is converted to the monoamide having an actual equivalent weight of 400 as a base. This compares favorably with the calculated value of 406 (388 plus a mole of free water present in the mixture).

Amides of hydroxyethyltrimethylamine and a branched-chain lanecosoic acid are obtained in a like fashion, starting with a cut of hexamer of propene and methylacrylate. Analysis shows the multiple branched-chain acid intermediate obtained to be 77% pure acid having an equivalent weight of 420. It is next converted to the effective amide additive of the invention by reacting it with hydroxyethyltrimethylammonium chloride. The monoamide product has an equivalent weight of 443 as compared with the theoretical value of 410 for a pure hexacosenyl monoamide.

The following Table I shows the results of several "Water Reaction" tests of gasoline compounded with a number of representative amidoamides of this invention. The base gasoline used in these tests was a conventional commercial leaded regular-grade gasoline, free of any other surfactant. The monoamide was added in a concentration of 250 p.p.m.

<table>
<thead>
<tr>
<th>Run</th>
<th>Acyl group of the amide</th>
<th>Time in minutes before separation of two distinct bright phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Trioleic acid produced by oxidizing alkylene hydroxides in the reaction of CO and propene tetramer</td>
<td>3</td>
</tr>
<tr>
<td>2.</td>
<td>Oxidized acids produced by reacting propene pentamer with methylacrylate</td>
<td>10</td>
</tr>
<tr>
<td>3.</td>
<td>Hexacosene acids produced by reacting propene hexamer with methylacrylate</td>
<td>From 10-30</td>
</tr>
<tr>
<td>4.</td>
<td>Naphthenic acids</td>
<td>About 15</td>
</tr>
<tr>
<td>5.</td>
<td>Rosin acids</td>
<td>About 30</td>
</tr>
</tbody>
</table>
In all instances, a perfect phase separation and a clear gasoline phase were obtained without any cloud or floc remaining in less than one hour. This rapid clean separation into a bright gasoline phase and a clear water phase represented an unexpected improvement as compared with the results obtained with other otherwise excellent additive, namely, monooleamide of hydroxyethyl ethylene diamine, which, when used in the same concentration, imposed a delay of at least several hours for the separation of emulsion and disappearance of haze.

A similar improvement was observed in Water Tolerance Tests which used other base gasoline fuels compounded with the amide additive of the invention, at either lower or higher concentrations.

Samples of the same base gasoline, compounded with representative aminoamide additives, as shown in Table I, were subjected to the "Glass Throttle Body Test" in order to confirm their effectiveness as deposit-reducing agents, particularly with reference to the deposits which occur in the throttle body section of the carburetor.

In this test a glass throttle body is inserted between the float section and the cast iron throttle body of a conventional carburetor. The throttle plate and shaft are removed from the cast iron body, and the shaft holes are bored out. The glass body is inserted in the place of glass tubing 1/4" thick, 1 1/4" in diameter and 2" long. Some 3/4" from the upper edge, holes are drilled diametrically in the tube to receive a conventional metal throttle plate and shaft. The carburetor and engine are those of a Plymouth automobile. Two small tubes carry the idle fuel mixture from the float section to appropriate passages in the cast iron throttle body.

In testing, the engine is run one hour on the base fuel without any detergent additive being present, at about 500 r.p.m. idle with full throttle, and no-load acceleration up to about 3,000 r.p.m. every 15 minutes, while the blowby is piped to the air cleaner above the carburetor. After one hour, the engine is made to operate on the same fuel but this time containing a specified amount of the deposit-removing additive. Before beginning this second phase of the test, the glass body is photographed to record the appearance of deposits formed in the first hour of running. Then the glass body is reinstalled without removing the deposits. The engine is run again for four hours without returning blowby to the air cleaner. Finally, the engine is shut down, the glass body is removed, and the percentage of deposits removed in this phase of the test is determined. This procedure is designated "Clean-Up Procedure."

In a representative run, the same base gasoline, that is, a commercial leaded, regular-grade gasoline was used. The amide was a monoamide of hydroxyethyl ethylene diamine and multiple branched-chain aliphatic acids produced by reacting propene pentamer with methylacrylate. The concentration employed was 30 p.p.m. The percentage of "clean-up" observed after the termination of the run was 53%. This figure represented an average of a six-run series.

In another test series, we used the same gasoline and a monoamide additive of hydroxyethyl ethylene diamine and aliphatic naphthenic acids from petroleum in a concentration of 50 p.p.m. The series consisted of six runs, and the average "clean-up" recorded was 56%. These two figures obtained in the "Glass Throttle Body Test" favorably compare with the 'clean-up' in the range of 40 to 60% obtainable with the oleic acid monoamide of hydroxyethyl ethylene diamine, recognized as satisfactory in the automobile engine practice.

In addition to being satisfactory as deposit-removing additives, the monoamides of our invention have the advantage of reducing the stalling of automobile engines due to ice formation in the carburetor. When used in the amounts specified, and preferably in amounts from 10 to 1,000 p.p.m., they enhance the operation of the engines under cool and humid atmospheric conditions.

It may be also added that the monoamides of this invention minimize ferrous corrosion which does occur when the metal parts of the engine come into contact with gasoline contaminated with moisture. The same action is exerted by them in fuel distribution systems, and thus they are applicable for preventing rusting of tanks, pipelines and tankers.

It behooves to mention at this point that salts of the effective aminoamides of our invention are likewise effective in reducing the deposits, preventing stalling, while being resistant to the formation of emulsions and haze when gasoline containing them is mixed with water. Among these salts, there may be mentioned carboxylates, in particular, salts of saturated C1-C4 aliphatic monocarboxylic acids. Likewise effective are various salts of phosphorus containing acids, such as oxyphosphorus acids and acids with one or two hydrocarbon radicals attached to the central phosphorus atom, e.g. phosphinic acids, phosphonic acids, and alkyl phosphoric and alkyl phosphonic acids. Particularly effective, both as regards the reduction of deposits and the resistance to emulsion formation are aminoamide salts of mono- and dialkylphosphoric acids of 8 to 20 carbon atoms in each of their alkyl radicals.

Ordinarily it is desirable to prepare and distribute the additives of the invention, whether in the form of amides or their corresponding salts, as concentrates, so as to facilitate handling and to enhance a simple blending operation when adding them to gasoline. In preparing these concentrates, gasoline-compatible organic solvents having substantially the same boiling range of the gasoline, for instance, liquid hydrocarbon solvents or alcohols, may be used. Examples of hydrocarbon solvents are aromatic solvents, while examples of alcohols are C5-C8 aliphatic alcohols, such as isobutanol, n-butanol, methylisobutylcarbinol, and the like. The additive is dissolved in such solvents within a wide range of concentrations from at least 10 up to at least 70% by weight. Before concluding this description, it is to be pointed out that the gasoline compositions compounded with the particular amides in accordance with the invention may contain other conventional gasoline additives in customary minor amounts, provided such additives do not interfere with or take away the advantages imparted by the amide additives. Among such additional materials which may be present in the gasoline there may be mentioned lead antiknock agents, such as tetraethyl lead, lead scavengers, dyes, inhibitors of spark plug fouling, oxidation inhibitors, and so forth. An additional improvement is achieved by introducing into the gasoline compounded with the additives of the invention a non-volatile oil, for instance, a light mineral lubricating oil or a petroleum spray oil. These oils act as carriers for the engine deposits dissolod by the action of the amide additive of our invention. One may incorporate from about 0.05 to about 0.5% by volume of such carrier oils in the gasoline.

It is to be understood that the invention is by no means limited to the particular examples offered in illustration thereof and by the recitals of any representative materials, but that many modifications, which come within the spirit and scope of the invention as defined in the following claims, are intended to be included in the definitions of these claims.

1 claim:

What is claimed is:

1. An improved engine fuel for use in spark-ignition engines, comprising a major proportion of gasoline, and, in combination therewith, a small amount of from about 0.001 to about 0.1% by weight of an oil-soluble, emulsion-resistant monoamide product of reaction of a polyamine from the group of C2-C10 alkylen polyamines and hydroxy-terminated C2-C10 alkylen polyamines with a hydrocarbon monocarboxylic acid from the group of aliphatic C15-C20 hydrocarbon monocarboxylic acids with at least 2 alkyl groups branching off the main carbon
chain of the acyl portion thereof and alicyclic C_{15}-C_{20} hydrocarbon monocarboxylic acids.

2. An engine fuel as defined in claim 1 wherein said oil-soluble monoamide is present as a salt thereof from the group of salts of phosphorus-containing acids and saturated C_{2}-C_{9} aliphatic monocarboxylic acids.

3. An additive concentrate intended for incorporation into gasoline, consisting essentially of an organic, gasoline-compatible solvent boiling in the gasoline range and selected from the group of hydrocarbon solvents and C_{2}-C_{9} saturated aliphatic alcohols, and, dissolved in said solvent, from about 10 to about 70% by weight of an oil-soluble, emulsion-resistant monoamide of a polyamine from the group of C_{2}-C_{10} alkylene polyamines and hydroxy-terminated C_{2}-C_{10} alkylene polyamines, and a hydrocarbon monocarboxylic acid from the group of aliphatic C_{15}-C_{30} hydrocarbon monocarboxylic acids with at least two alkyl groups branching off the main carbon chain of the acyl portion thereof and alicyclic C_{15}-C_{20} hydrocarbon monocarboxylic acids.

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